



Quality Assurance Project Plan (QAPP)	2010
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Statewide Stream Pollution Trends Monitoring Program

May 2010



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Statewide Stream Pollution Trends Monitoring Program

Quality Assurance Project Plan

Surface Water Ambient Monitoring Program

**Revision 1
May 2010**

GROUP A ELEMENTS: PROJECT MANAGEMENT

1. TITLE AND APPROVAL SHEETS

PROJECT NAME: Surface Water Ambient Monitoring Program (SWAMP) Statewide Stream Pollution Trends (SPoT) Monitoring

DATE: May 19, 2010

NAME OF RESPONSIBLE ORGANIZATION: University of California, Davis
Marine Pollution Studies Laboratory
Granite Canyon (UCD-MPSL)


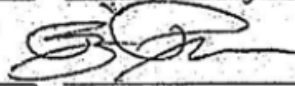
Quality Assurance Project Plan (QAPP) Revision Number: v1

Acknowledgements

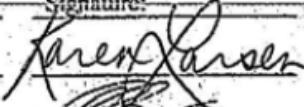

The Project Manager and Project Quality Assurance Officer would like to thank the following individuals for their contributions to this document: Matthew Gomes, SWAMP QA Team, Katie Siegler, UC Davis, Autumn Bonnema, Moss Landing Marine Laboratories, and Rich Gossett, California State University Long Beach.

APPROVAL SIGNATURES

GRANT ORGANIZATION:

<u>Title:</u>	<u>Name:</u>	<u>Signature:</u>	<u>Date:</u>
Project Manager (PM)	John Hunt		6/18/10
Quality Assurance (QA) Officer	Bryn Phillips		6/18/10

STATE WATER RESOURCES CONTROL BOARD:

<u>Title:</u>	<u>Name:</u>	<u>Signature:</u>	<u>Date:</u>
Contract Manager	Karen Larsen		22 June 2010
SWAMP QA Officer	Beverly van Buren		06/21/10

2. TABLE OF CONTENTS

	Page:
Group A Elements: Project Management	2
1. Title and Approval Sheets; Acknowledgements	2
2. Table of Contents.....	4
3. Distribution List.....	6
4. Project/Task Organization	6
5. Problem Definition/Background.....	9
6. Project/Task Description	10
7. Quality Objectives and Criteria for Measurement Data.....	11
8. Special Training Needs/Certification.....	13
9. Documents and Records	13
Group B Elements: Data Generation and Acquisition	14
10. Sampling Process Design	14
11. Sampling Methods.....	16
12. Sample Handling and Custody	16
13. Analytical Methods.....	18
14. Quality Control.....	19
15. Instrument/Equipment Testing, Inspection, and Maintenance.....	20
16. Instrument/Equipment Calibration and Frequency	21
17. Inspection/Acceptance of Supplies and Consumables.....	21
18. Non-Direct Measurements (Existing Data)	21
19. Data Management.....	21
Group C Elements: Assessment and Oversight	22
20. Assessments & Response Actions	22
21. Reports to Management.....	22
Group D Elements: Data Validation and Usability.....	23
22. Data Review, Verification, and Validation Requirements.....	23
23. Verification and Validation Methods	23
24. Reconciliation with User Requirements	23

LIST OF APPENDICES

APPENDIX A. Standard Operating Procedures (SOPs) for Conducting Field Collections of Bed Sediment Samples at Watershed Integrator Sites in the Surface Water Ambient Monitoring Program (SWAMP) Stream Pollution Trend (SPoT) Program.....	25
APPENDIX B. Marine Pollution Studies Laboratory Chain of Custody Form.....	34
APPENDIX C. Sampling Equipment Cleaning Standard Operating Procedure.....	35

LIST OF FIGURES

Figure 1. Organizational chart.	8
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LIST OF TABLES

Table 1. (Element 4) Personnel Responsibilities.....	7
Table 2. (Element 7) Data Quality Indicators.....	11
Table 3. (Element 12) Sample Handling and Custody.....	17
Table 4. (Element 13) Analytical Methods.....	19

3. DISTRIBUTION LIST

<u>Title:</u>	<u>Name:</u>	<u>Tel. No.:</u>	<u>QAPP No*:</u>
Contractor PM	John Hunt	(831) 684-1203	1
Contractor QA Officer	Bryn Phillips	(831) 624-0947	2
State Board Contract Manager	Karen Larsen	(916) 464-4646	3
State Board QA Officer	William Ray	(916) 341-5583	4
Organic Chemistry Lab Manager	Rich Gossett	(562) 985-2469	5
Metals Chemistry Lab Manager	Autumn Bonnema	(831) 771-4175	6
Grain Size Lab Manager	Frank Shields	(831) 724-5422	7
SWAMP QA Officer	Beverly van Buuren	(206) 297-1378	8

4. PROJECT/TASK ORGANIZATION

4.1 Involved Parties and Roles

The UCD-MPSL conducts contaminant studies in urban and agricultural watersheds. As the project lead, UCD will organize the sample collection, field and in-house analysis of samples, and the initiation and maintenance of contracts with contract laboratories for analysis of organic chemistry, trace metals, total organic carbon (TOC), and grain size.

John Hunt (UCD) will be the PM and will oversee all aspects related to planning and timely completion of the project. This includes organization of field staff, scheduling of sampling days, management of the UCD-MPSL in-house laboratory, and interactions with the contract laboratory.

Bryn Phillips is the QA Officer, detailed below in Section 4.2.

California State University, Long Beach (CSULB) will be the contract laboratory for all organic chemical analyses of samples, TOC, and grain size analyses. CSULB will analyze submitted samples in accordance with all QA requirements found in the *Surface Water Ambient Monitoring Program Quality Assurance Program Plan* (QAPrP).

The Moss Landing Marine Laboratory Marine Pollution Studies Laboratory (MLML-MPSL) will be the contract laboratory for all trace metal analyses. The MLML-MPSL will analyze submitted samples in accordance with all method and QA requirements found in the QAPrP.

Table 1. (Element 4) Personnel Responsibilities

Name	Organizational Affiliation	Title	Contact Information (Telephone number, fax number, email address.)
John Hunt	UC Davis-MPSL	PM and Toxicity Lab Director	(831) 684-1203 (831) 684-1203 (f) jwhunt@ucdavis.edu
Bryn Phillips	UC Davis-MPSL	QA Officer and Data Manager	(831) 624-0947 (831) 626-1518 (f) bphilips@ucdavis.edu
Rich Gossett	CSULB	Organic Chemistry Analyses	richgossett@yahoo.com
Autumn Bonnema	MLML-MPSL	Trace Metals Analyses	(831) 771-4175 (831) 633-0128 (f) bonnema@mlml.calstate.edu
Russell Fairey	MLML	Contract and Financial Manager	(831) 771-4161 (831) 633-0805 (f) fairey@mlml.calstate.edu

4.2 Quality Assurance Officer Role

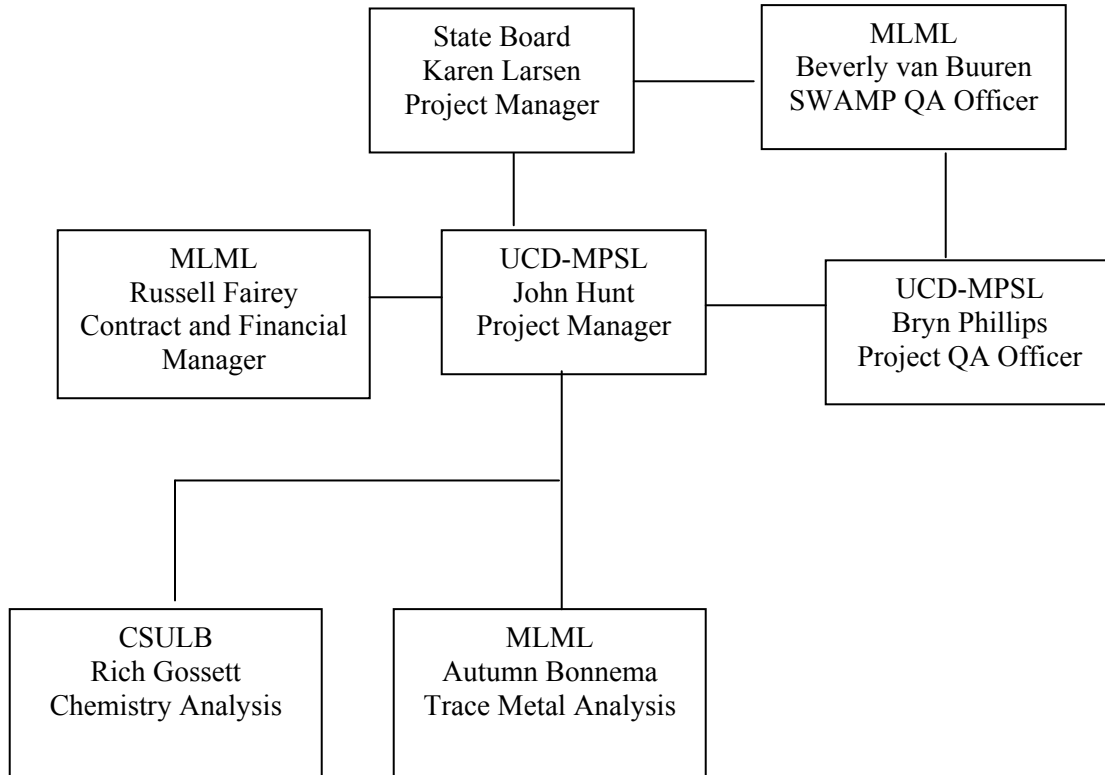
Mr. Phillips will review all project data. He is responsible for ensuring that all QA parameters are met, including field sampling and transport, laboratory storage, and laboratory testing. Mr. Phillips plays an advisory role in all aspects of data collection and reporting, and has been the QA Officer on a number of UCD projects. Mr. Phillips will coordinate with Rich Gossett of CSULB and Autumn Bonnema of MLML-MPSL to ensure appropriate QA measures are upheld.

4.3 Persons Responsible for Quality Assurance Project Plan Update and Maintenance.

John Hunt and Karen Larsen will maintain and update the approved quality assurance project plan (QAPP) as needed. Either person can make changes to the QAPP with approval of the Project QAO and the SWAMP QAO.

4.4 Organizational Chart and Responsibilities

Figure 1. Organizational chart.



5. PROBLEM DEFINITION/BACKGROUND

5.1 Problem Statement

Pesticides and other contaminants have been found in streams and estuaries throughout California at levels that exceed Basin Plan numerical objectives. Agriculture, industry, urban and residential areas, mining operations, and other land uses contribute polluted runoff to these waterways while aquatic communities may be affected by the transport of contaminants from watershed areas into streams and downstream habitats. Stream conditions are also expected to be affected by environmental and resource agency management actions designed to improve water quality. The SPoT program at watershed integrator sites is SWAMP's statewide program to measure trends in contaminants and their effects, and to link these trends to changes in land use and resource management activity.

The SPoT program is also specifically designed to serve as a statewide network of sites that can link together local monitoring efforts by stormwater agencies, Total Maximum Daily Load (TMDL) programs, agricultural waiver programs, regional monitoring, and others to provide a statewide context for local monitoring. This makes it possible to compare among local areas and regions, to indicate the relative magnitude of problems, and to gauge the success of management programs. A SPoT field survey document Standard Operating Procedures (SOPs) for Conducting Field Collections of Bed Sediment Samples at Watershed Integrator Sites in the Surface Water Ambient Monitoring Program (SWAMP) Stream Pollution Trend (SPoT) Program has been developed to foster consistency of related monitoring efforts.

5.2 Decisions or Outcomes

This assessment of trends in contaminant concentrations and biological effects in California streams supports a number of agency priorities and statutory requirements, as well as general purpose assessment goals. Specific groups that will benefit from this trend monitoring program include:

1. Regional Board staff: tracking effectiveness of TMDL and management actions
2. State and Regional Board staff: program coordination and broad management context
3. Stormwater, agricultural waiver, and National Pollution Discharge Elimination System (NPDES) programs: broad context for management
4. State Board and Environmental Protection Agency (EPA) staff: Clean Water Act (CWA) §305(b) reporting
5. State Board and EPA Non-point source programs: evaluating changes in water quality
6. State and Regional Board staff: identifying emerging contaminants
7. Public constituencies: prioritizing policy needs

5.3 Water Quality or Regulatory Criteria

This project is designed primarily to assess support for aquatic life beneficial uses of California streams through analysis of sediments. This QAPP is complementary to the 2008 SWAMP QAPrP, and provides additional guidance and an updated protocol for sampling sediments in depositional areas of streams surveyed in this program. Additionally, the 2008 SWAMP QAPrP can be referred to for criteria for sediment chemical analysis, sediment trace metal analysis, ancillary measures, and sediment toxicity.

6. PROJECT/TASK DESCRIPTION

6.1 Work Statement and Produced Products

Depositional sediments will be collected near the bases of large heterogeneous watersheds. Approximately 100 sites will be sampled annually. All sediment samples will be tested for toxicity and will be analyzed for trace metal and organic chemicals. A subset of mostly urban samples, described below in 6.2, will have additional analyses performed.

There will be coordination with cooperating programs to facilitate monitoring of additional parameters that enhance the information value of each survey.

A bi-annual interpretive report and fact sheet will be produced, describing trends in contaminant concentrations and biological effects in large watersheds throughout California. Data collected will also contribute to 305(b) reporting and 303(d) listing. Data will be disseminated through the SWAMP database for collaborating programs and public use.

6.2. Constituents to be Monitored and Measurement Techniques

Sediment samples will be collected according to the attached Standard Operating Procedures (SOPs) for Conducting Field Collections of Bed Sediment Samples at Watershed Integrator Sites in the Surface Water Ambient Monitoring Program (SWAMP) Stream Pollution Trend (SPoT) Program (Appendix A). Sediment at each site will be collected from 5-10 depositional areas within a 100m reach of the stream in order to adequately characterize the quality of sediments delivered to the stream by runoff throughout the watersheds.

Sediment toxicity will be assessed using the 10-d growth and survival protocol for *Hyalella azteca*, as described in the SWAMP QAPrP. Toxicity tests will provide data to estimate biological effects of contaminants.

At each of these sites, samples will be analyzed for trace metals, pesticides, polychlorinated biphenyls (PCBs), total phosphorus, TOC and sediment grain size. All measurements are considered critical to the assessment. At a subset of urban sites, polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs) will also be measured.

6.3 Project Schedule

All sites will be sampled as part of a continuous monitoring effort, beginning in 2008. Sites will be sampled during base flow or near-base flow conditions following annual peak flows. Sampling should occur before significant contaminant breakdown occurs via hydrolysis or photolysis. Surveys will be scheduled based on regional hydrologic cycles, with Southern California coastal streams sampled in spring, and other regions sampled progressively later in the year as stream flows recede.

Each calendar year's field work and toxicity testing will be complete by November 15th of that year. Chemical analyses will be completed by October 15th of the following year, along with data submissions to the SWAMP database by November 1st of the following year. For example, sampling and toxicity testing completed by 11/15/2010 will have chemistry completed by 10/15/2011, and data submitted to the SWAMP database by 11/1/2011.

6.4 Geographical Setting

All sites in the assessment will be located in the State of California. Sites will be selected in waterbodies at points where contaminants released throughout large watersheds are likely to accumulate. Design of integrator sampling sites will include approximately 100 sites throughout the state, which is roughly divided in to 135 major hydrologic units. Sites will be chosen each year based on funding availability and are subject to change; therefore a complete list of sites is not included in this QAPP. A list of current and previous sites can be requested from PM John Hunt.

6.5 Constraints

All sampling designs, timelines, and suites of analyses are dependent on adequate funding.

7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

Data quality indicators (DQIs - i.e., precision, bias, representativeness, completeness, comparability, and sensitivity) and criteria for measurement data are outlined below.

Table 2. (Element 7) Data Quality Indicators

<u>Measurement or Analyses Type</u>	<u>Applicable Data Quality Indicators</u>
Sediment Toxicity	meet acceptability criteria relative to reference toxicant tests, ancillary test condition measures, and completeness
Sediment grain size and TOC	accuracy, precision, comparability, completeness, sensitivity
Sediment Trace Metals	accuracy, precision, comparability, completeness, sensitivity
Sediment Trace Organics	accuracy, precision, comparability, completeness, sensitivity

Accuracy will be determined by measuring one or more certified reference materials or standard reference materials. At least one reference sample per batch of 20 samples is required. Additional analyte recovery measurements may be made by laboratory spiking of a replicate sample with a known concentration of the analyte. The target level of addition is targeted to be at least twice the original sample concentration.

Precision measurements will be determined on field and/or laboratory replicates. At least one replicate per batch of 20 samples is required. The relative percent difference (RPD) between two replicate samples or the relative standard deviation (RSD) between more than two replicate samples will be less than the MQOs listed in the SWAMP QAPrP for each analyte of interest. Following are the calculations:

$$\text{RPD} = \text{ABS (rep 1 - rep 2)} \times 100 / \text{Average (rep 1, rep 2)}$$

$$\text{RSD} = \text{STDEV (all replicate samples)} \times 100 / \text{Average (all replicate samples)}$$

ABS is the absolute value

STDEV is the standard deviation

Comparability is necessary so that data derived from this project can be combined with data from other projects. Such combinations are useful for wider scale assessments, such as between regions or between different time periods. The standard for data comparability will be the ability to enter the data into the statewide SWAMP database, so that it can be integrated with high quality data from other studies. Data from previous studies will not be used for analyses in this study, and no acceptance criteria for previous data are identified. Data from this project will be generated using SWAMP comparable QA and quality control (QC) procedures for performance based methods, including all necessary standards, blanks, and reference materials. All data reported for this project will be produced according to this QAPP and will be SWAMP-comparable.

Representativeness is a qualitative measure of the degree to which the sampling approach characterizes the target population.

Completeness is a measure of the number of analyses generating useable data for each analysis divided by the number of samples collected for that analysis. Based on past experience with numerous projects of this type, we expect to produce acceptable data from greater than 95% of the samples collected.

Method sensitivity is measured as the method detection limit. These limits are sensitive enough to resolve biologically relevant differences in ambient chemical concentrations.

Suggested Standard Reference Material:

Grain size: National Institute of Standards and Technology (NIST) 1003b glass spheres (8 to 58 um diameter), constant-density spheres having a range of diameters. Precision and accuracy of the sedigraph (particle size analyzer) is evaluated with a garnet standard reference material (SRM - Micromeritics, Inc.).

TOC: laboratory control material

Trace Elements: National Research Council (NRC) MESS-3 or NIST 1646

Trace Organics: NIST 1941a or similar

Field and Laboratory Measurement Quality Objectives Tables

All MQO tables for field and laboratory data are included in the 2008 SWAMP QAPrP for the following parameters:

Sediment Trace Metals, including Hg and As: Table A5 of the 2008 SWAMP QAPrP

Synthetic Organic Compounds: Table A8 of the 2008 SWAMP QAPrP

Sediment TOC: Table A4 of the 2008 SWAMP QAPrP

Sediment Grain Size: Table A4 of the 2008 SWAMP QAPrP

10-day *Hyaella azteca* Sediment Toxicity test: Table A14 of the 2008 SWAMP QAPrP

8. SPECIAL TRAINING NEEDS/CERTIFICATION

8.1 Specialized Training or Certifications

No specialized training or certifications are required for this project. The main subcontractor will conduct field surveys and water and sediment toxicity analyses (UCD-MPSL, Contact: John Hunt). UCD-MPSL is the primary toxicology laboratory for SWAMP. In cooperation with CDFG-MPSL, UCD-MPSL authored the toxicology section of the SWAMP QAPrP. Sediment toxicity test methods follow standard EPA procedures.

Sediment chemistry for organic contaminants, TOC, and grain size will be analyzed by CSULB (Contact: Rich Gossett). Trace metals will be analyzed by MPSL-MLML (Contact: Autumn Bonnema).

8.2 Training and Certification Documentation

A complete listing of laboratory accreditation certificates is available directly from the subcontractors.

8.3 Training Personnel

No new training is required for this project. Training records for individual laboratory tasks are maintained at laboratories and are available upon request.

9. DOCUMENTS AND RECORDS

The following documents, records, and electronic files will be produced:

- QAPP (submitted to contract manager in paper and electronic formats)
- Monitoring Plan (submitted to contract manager in paper and electronic formats)
- Field Sampling Sheets (internal documentation available upon request)
- Chain of Custody (COC) Forms (exchanged for signatures with chemistry lab and kept on file)
- Lab Sample Disposition Logs (internal documentation available upon request)
- Calibration Logs for measurements of water quality standards (internal documentation available upon request)
- Refrigerator Logs (internal documentation available upon request)

- Meter and Spectrophotometer Maintenance Logs (internal documentation available upon request)
- Test Organism Culture Logs (internal documentation available upon request)
- Culture Water Lot Logs (internal documentation available upon request)
- Pipette Calibration Logs (internal documentation available upon request)
- Thermometer Calibration Logs (internal documentation available upon request)

An Annual Interpretive Report will be submitted by October 31, 2010. After this initial report, Biannual Interpretive Reports will be due on December 31st of alternating years. Reports will be submitted to the contract manager in electronic format.

Copies of this QAPP will be distributed by the PM to all parties directly involved in this project. Any future amended QAPPs will be distributed in the same fashion. All originals of the first and subsequent amended QAPPs will be held at UCD-MPSL. Copies of versions, other than the most current, will be discarded so as not to create confusion.

Biannual Interpretive Reports will be provided to State Board PM Karen Larsen. Reports will include summary data tables and an appendix that contains all project data in electronic SWAMP compatible spreadsheet format. All laboratory logs and data sheets will be maintained at MPSL for five years following project completion, and are available for review by the Contract Manager or designee during that time. Copies of reports will be maintained at UCD-MPSL for five years after project completion then discarded, except for the database, which will be maintained without discarding. Back up records of data will be maintained on an external hard drive offsite from the laboratory. Laboratories will provide electronic copies of tabulated analytical data (including associated QA/QC information outlined below) in the SWAMP database format or a format agreed upon by the Contract Manager and the UCD-MPSL Project/Data Manager or designee.

GROUP B: DATA GENERATION AND ACQUISITION

10. SAMPLING PROCESS DESIGN

The SPoT program is designed to survey watersheds throughout the State of California to determine long-term trends in stream pollution and their relationships with land use and resource management activities within the watershed. The program has three primary goals:

1. To determine long-term trends in stream contaminant concentrations and their biological effects statewide;
2. To relate water quality indicators to land-use characteristics and to the effectiveness of agency management efforts; and
3. To establish a network of sites throughout the state to serve as a backbone for collaboration with local, regional, & federal monitoring programs.

The sampling design is based on the United States Geological Survey's (USGS') National Water Quality Assessment (NAWQA) program concept of selecting targeted integrator sites near the discharge points of large watersheds, where contaminant-bearing sediments are deposited by hydrologic processes within the watersheds and main stream systems. There are 135 USGS 8-digit hydrologic units (called cataloging

units) in California. These are large watersheds such as drained by the Russian, South Fork American, Salinas, or Santa Clara Rivers. The SPoT program is designed to sample approximately 100 watersheds of this size, depending on land use intensity and resource management importance. The third goal of the program is addressed by targeting some of the 100 sites in smaller watersheds important for local and regional monitoring programs, such as those directed by stormwater agencies and coalitions, irrigated lands programs, and Regional monitoring programs. By co-locating sampling sites with local programs, SPoT provides statewide perspective for local programs, as well as local enhancement and detail to the statewide program.

Sites are originally selected based on hydrology, land use, and the needs of partner programs. The sites are then visited for reconnaissance to find a 100-m reach within which there are at least five to ten depositional areas from which fine-grained sediment can be collected. To select adequate reaches, the actual sampling location can be moved 1 km or more upstream or (usually) downstream of the original target site. This is warranted because the program goals are to characterize pollution activity within the watershed, not to characterize the condition of a specific site.

Subsamples collected from the five to ten depositional areas are homogenized to create a sample representative of depositional sediment mobilized within the watershed. Care is taken to sample recent sediment deposits in active areas of the stream bed and to avoid banks, benches, and other areas where sediment may have been deposited more than one year previously. Sediment is sampled to a depth of up to 5 cm if the entire 5 cm core is homogeneous and appears to have been deposited within the same hydrologic cycle of seasonal high water receding to annual base flow. Surficial sediment as shallow as 1 cm may need to be collected if there is clear layering indicating deposition over multiple annual cycles.

Sediment samples will be collected according to the attached Standard Operating Procedures (SOPs) for Conducting Field Collections of Bed Sediment Samples at Watershed Integrator Sites in the Surface Water Ambient Monitoring Program (SWAMP) Stream Pollution Trend (SPoT) Program (Appendix A). The general procedure for collection of bed sediment is detailed on page 7 of the SOP. Procedures for processing bed sediment samples, once they are collected, are detailed on page 9 of the SOP.

Sites will be sampled annually on an ongoing basis, beginning in 2008. Sites will be sampled during base flow or near-base flow conditions following annual peak flows. Sampling should occur before significant contaminant breakdown occurs via hydrolysis or photolysis. Surveys will be scheduled based on regional hydrologic cycles, with Southern California coastal streams sampled in spring, and other regions sampled progressively later in the year as stream flows recede.

For this project, no field data will be collected and all lab data is critical and of equal importance.

Natural variability in sediment contaminant concentrations is expected. Variability is addressed by compositing sediment from 5 to 10 depositional areas in the 100-m reach that comprises each watershed site. Spatial and temporal variability will be characterized through pilot studies, beginning in 2010, in which three or more additional reaches will be sampled in a subset of watersheds. This survey of four reaches per watershed will be repeated during each of three seasons.

Bias can be introduced by the timing, reach selection, and depositional area selection of the surveys. Bias is addressed by training field crews to identify and sample the finest sediment available in the lowest gradient (calmest) reaches, since the fine sediments are the targeted transport medium for contaminants. Seasonal bias is addressed by timing the surveys based on regional hydrologic cycles and conducting the surveys soon after base flows are established following annual high flows for all watersheds.

11. SAMPLING METHODS

Please see the attached Standard Operating Procedures (SOPs) for Conducting Field Collections of Bed Sediment Samples at Watershed Integrator Sites in the Surface Water Ambient Monitoring Program (SWAMP) Stream Pollution Trend (SPoT) Program (Appendix A).

If suitable depositional areas for collecting sediments cannot be found at a target site, the project scientist (John Hunt or designee) may decide to search the general area for an alternate integrator site where fine sediment is deposited. If an alternate location is sampled, the project scientist will notify collaborating institutions (Regional Monitoring Coordinators, stormwater agencies, etc.) of the change in location. This may result in renaming of the site, and may affect trends analyses. If no suitable depositional areas can be found, sampling personnel should not collect the sediment sample and should discuss alternatives with the project scientist and collaborators. In this case, a note is added to the cruise report so that the missing sample is accounted for in the reconciliation of monitoring events. Sites that are consistently difficult to sample should be considered for elimination or relocation from the survey schedule if appropriate.

All sampling equipment and cleaning processes are identified in the attached SOP, with details on the cores, scoops, and mechanical grab samplers on pages 7-8. Waste acid and waste solvent created in the field will be collected in separate containers for neutralization and disposal at MPSL.

12. SAMPLE HANDLING AND CUSTODY

Sample containers are cleaned and prepared by the analyzing laboratory, or are factory pre-cleaned. Each container is given a permanent sample label written in waterproof ink. At a minimum, each sample label includes station name and code, sample date, Lab identification (ID), analysis required, and collector's initials.

It is critical that sample contamination be avoided during collection. All sampling equipment is composed of a non-contaminating material and is thoroughly cleaned before each use as described in Appendix C of MPSL SOP 1.3 (Puckett, M. Quality Assurance Management Plan for the State of California's Surface Water Ambient Monitoring Program; California Department of Fish and Game, Monterey, CA, 2002). Sampling personnel wear nitrile gloves whenever taking or processing samples to avoid contact contamination. In addition, airborne contamination is avoided by keeping sample containers appropriately covered when not in use. Sampling methods follow those outlined in the Standard Operating Procedures (SOPs) for Conducting Field Collections of Bed Sediment Samples at Watershed Integrator Sites in the Surface Water Ambient Monitoring Program (SWAMP) Stream Pollution Trend (SPoT) Program (Appendix A).

Approved sampling methods described in the SOP include the use of hand cores, long cores, sediment scoops, and sediment grabs.

Summary of Sample Container, Volume, Preservation, and Storage Requirements for Bed Sediment Samples (for contaminant analysis)

Table 3. (Element 12) Sample Handling and Custody

Parameters for Analysis	Recommended Containers	Typical Sample Volume (mL)	Initial Field Preservation	Maximum Holding Time
Bed Sediment Samples				
Trace Metals, including Hg and As (except for Se--see below)	60-mL I-Chem 300-series clear glass jar with Teflon lid-liner; Pre-cleaned	60 mL (one jar)	Cool to 4 °C, dark, up to 14 days	12 months ⁽¹⁾ (-20 °C)
Selenium (separate container required)	60-mL I-Chem 300-series clear glass jar with Teflon lid-liner; Pre-cleaned	60 mL (one jar)	Cool to 4 °C, dark, up to 14 days	12 months ⁽¹⁾ (-20 °C)
Synthetic Organic Compounds	250-mL I-Chem 300-series amber glass jar with Teflon lid-liner; Pre-cleaned	500 mL (two jars)	Cool to 4 °C, dark, up to 14 days	12 months ⁽¹⁾ (-20 °C)
Sediment TOC	250-mL ⁽³⁾ clear glass jar; Pre-cleaned	125 mL (one jar)	Cool to 4 °C, dark, up to 28 days	12 months ⁽²⁾ (-20 °C)
Sediment Grain Size	250-mL ⁽³⁾ clear glass jar; Pre-cleaned	125 mL (one jar)	Cool to 4 °C, dark, up to 28 days	28 days (4 °C) <i>Do not freeze</i>
Sediment Toxicity Testing	1-L I-Chem wide-mouth polyethylene jar with Teflon lid-liner; Pre-cleaned	2 (two jars filled completely)	Cool to 4 °C, dark, up to 14 days	14 days (4 °C) <i>Do not freeze</i>
<p>(1) Sediment samples for parameters noted with one asterisk (*) may be refrigerated at 4 °C for up to 14 days maximum, but analysis <u>must</u> start within the 14-day period, or the sediment sample <u>must</u> be stored frozen at minus (-) 20 °C for up to 12 months.</p> <p>(2) Sediment samples for sediment TOC analysis can be held at 4 °C for up to 28 days, and <u>should</u> be analyzed within this 28-day period, but can be frozen at any time during the initial 28 days, for up to 12 months at minus (-) 20 °C.</p> <p>(3) Sediment samples for TOC and grain size analysis can be combined in one 250 mL clear glass jar, and sub-sampled at the laboratory in order to utilize holding time differences for the two analyses. If this is done, the 250 mL combined sediment sample must be refrigerated only (<u>not frozen</u>) at 4 °C for up to 28 days, during which time the sub-samples must be aliquoted in order to comply with separate storage requirements (as shown above).</p>				

The sample collection form (the SWAMP COC form), coupled with a COC record and a laboratory analysis record, allows tracing of the complete history of a sample from time of collection to final entry of data to a computer database.

Samples will be shipped in insulated coolers. All caps and lids will be checked for tightness prior to shipping.

All samples will be handled, prepared, transported, and stored in a manner so as to minimize bulk loss, analyte loss, contamination, or biological degradation, according to the SOP (Appendix A). Sample containers will be clearly labeled with an indelible marker.

Ice chests are sealed with tape before shipping. Samples are placed in the ice chest with enough dry or wet ice to completely fill the ice chest. Forms are placed in an envelope and taped to the top of the ice chest or they may be placed in a Ziploc plastic bag and taped to the inside of the ice chest lid. It is assumed that samples in tape-sealed ice chests are secure whether being transported by staff vehicle, by common carrier, or by commercial package delivery.

The receiving laboratory has a sample custodian who examines the samples for correct documentation, proper preservation, and holding times. In this study, sample collection will be done by UCD-MPSL personnel, so samples will not change custody between field collection and laboratory storage. For all samples transported from MPSL to other labs, temperature will be checked at the receiving lab by pouring a small amount of sample into a beaker and immediately measuring with a thermometer.

Contract laboratories will follow sample custody procedures outlined in their QA plans. Contract laboratory QA plans are on file with the respective laboratories.

All samples remaining after successful completion of analyses will be disposed of properly only after written confirmation from the UCD-MPSL PM, John Hunt, that data have been received, reviewed and validated.

It is the responsibility of the personnel of each analytical laboratory to ensure that all applicable regulations are followed in the disposal of samples or related chemicals.

Project COC procedures require that possession of samples be traceable from the time the samples are collected until completion and submittal of analytical results. A complete COC form is to accompany the transfer of samples to the analyzing laboratory and to be forwarded to the UCD-MPSL PM, John Hunt, with the data reporting package. The COC is attached as Appendix B.

13. ANALYTICAL METHODS

Reporting Limits recommended for SWAMP programs are defined in Appendix C of the 2008 SWAMP QAPrP. A list of SOPs and methods are listed below in Table 4, *Analytical Methods*. All instrumentation can be found in said SOPs.

Field and laboratory analytical methods, including toxicity testing, follow protocols defined in the 2008 SWAMP QAPrP.

For analyses at UCD-MPSL, laboratory instruments and equipment will be calibrated and maintained by MPSL staff, under direction of Bryn Phillips, according to laboratory protocol in the following SOPs (Table 5). All calibrations and corrective actions are documented in logbooks for each instrument or piece of equipment. Data will be entered into the SWAMP database no more than three months from test termination as listed in the *Data Handling* SOP.

For analyses at MLML-MPSL, method specific criteria, corrective action procedures, and documentation for analyses can be found in the project QAPP or method. Data should be completed and reported within six months of sample receipt and within holding times.

For analyses at CSULB, all method specific criteria, corrective action procedures, and documentation for analyses can be found in the lab SOPs or the lab QAP. Analyses will be completed in 10-15 business days.

Table 4. (Element 13) Analytical methods

Analyte	Laboratory / Organization	Project Action Limit (units, wet or dry weight)	Project Reporting Limit (units, wet or dry weight)	Analytical Method	
				Analytical Method/ SOP	Modified for Method yes/no
Hyaella azteca 10-d	UCD-MPSL	NA	NA	US EPA (2000) 600/R-99/064 SOP 2.7	None
Alkalinity	UCD-MPSL	NA	NA	Digital Titration SOP 3.1	None
Dissolved Oxygen (DO), pH, Conductivity	UCD-MPSL	NA	NA	Accumet SOP 3.13	None
Ammonia	UCD-MPSL	NA	NA	Hach DR/2010 Spectrophotometer SOP 3.2	None
Diazinon and Chlorpyrifos	UCD-MPSL	NA	NA	ELISA SOP 3.3	None
Hardness	UCD-MPSL	NA	NA	Digital Titration SOP 3.5	None
Trace Metals	MLML-MPSL	NA	NA	Modified EPA 3052M followed by EPA 200.8	Yes for digestion
Mercury	MLML-MPSL	NA	NA	MPSL-107 followed by MPSL-103	None
Trace Organics	CSULB	NA	NA	EPA 3540C followed by EPA 8270D by EI-GCMS	Yes - Calibration checks differ
Pyrethroids, Toxaphene, and PBDEs	CSULB	NA	NA	EPA 3540C followed by EPA 8270D by NCI-GCMS	Yes – Uses NCI and calibration checks differ
TOC	CSULB	NA	NA	EPA 9060am	Yes – Uses TCD
Grain Size	CSULB	NA	NA	Plumb, 1981	None

14. QUALITY CONTROL

UCD-MPSL and contract laboratories will follow QC guidance provided in *Element B5: Quality Control* of the 2008 SWAMP QAPrP.

When control limits are exceeded, corrective actions will follow procedures listed in lab SOPs (Table 4) and Appendix D of the SWAMP QAPrP.

All procedures and formulas for calculating data quality indicators can be found in the introduction to QAPrP Appendix A. Five percent of the annual field samples collected will have field duplicates collected for analysis.

Laboratory Duplicates and Field Duplicates

$$RPD = \left| \frac{(V_{\text{sample}} - V_{\text{duplicate}})}{\text{mean}} \right| \times 100$$

Where:

v_{sample} : the concentration of the original sample

$v_{\text{duplicate}}$: the concentration of the duplicate sample

mean: the mean concentration of both samples

15. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

Laboratory instruments and equipment are inspected and maintained by UCD-MPSL laboratory personnel according to the manufacturer. Bryn Phillips, the Laboratory QA Officer, is responsible for equipment testing, inspection and maintenance. Testing, inspection, maintenance, and spare parts supply are conducted as described in the following SWAMP SOPs:

- 1.5 Standard Operating Procedure for Pipette Use
- 3.1 Standard Operating Procedure for Alkalinity Measurement
- 3.2 Standard Operating Procedure for Ammonia Measurement by Spectrophotometer
- 3.4 Standard Operating Procedure for Water Quality Meter (includes DO, pH, and conductivity)
- 3.5 Standard Operating Procedure for Hardness Measurement

All instruments and equipment have back-up components. If instruments do not pass inspection, back-up components are put in place. If it is determined that data have been recorded with faulty instruments the corrective action is to cross out the data on the data sheet, re-analyze the samples, and make a record of the occurrence.

For analyses at MLML-MPSL, all testing, inspection, and maintenance information is covered by the instrument manufacturer or the analytical method. All testing, inspection, and maintenance information at CSULB can be found in the specific lab SOPs or the general lab quality assurance plan (QAP).

16. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

Laboratory instruments and equipment will be calibrated and maintained by UCD-MPSL staff, under direction of Bryn Phillips, according to laboratory protocol and the following SWAMP SOPs. All calibrations and corrective actions are documented in logbooks for each instrument or piece of equipment.

- 1.5 Standard Operating Procedure for Pipette Use:
Pipette calibration is checked once per month. If pipettes are out of calibration, they are sent in for factory service.
- 3.1 Standard Operating Procedure for Alkalinity Measurement:
Alkalinity standards are checked quarterly. If standards do not read correctly, the digital titrator is replaced.
- 3.2 Standard Operating Procedure for Ammonia Measurement by Spectrophotometer

For analyses at MLML-MPSL, instrument and equipment calibration and frequency information is covered by the instrument manufacturer or the analytical method. All instrument and equipment calibration and frequency information at CSULB can be found in the specific lab SOPs or the general lab QAP.

17. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

All supplies and containers used in this study will be either certified for cleanliness (e.g. I-Chem jars), or thoroughly inspected prior to use (e.g. sampling gloves and equipment). Laboratories will determine that all supplies and consumables comply with acceptance criteria outlined in their Standard Operating Procedures prior to conducting analyses. Bryn Phillips, the laboratory QA Officer, is responsible for inspection and acceptance of supplies and consumables.

18. NON-DIRECT MEASUREMENTS (EXISTING DATA)

It is not anticipated that this study will use environmental measurements generated by other organizations.

19. DATA MANAGEMENT

The UCD-MPSL and each sub-contractor will be responsible for the study's data handling and storage. The data produced during this study will be managed following SWAMP protocols and be held in a SWAMP-compatible database at UCD-MPSL.

Chemistry and ancillary parameter data will be transferred to UCD-MPSL in Microsoft Excel spreadsheets and compiled into the database. Data will be reviewed to ensure that they are consistent with the format of the database and other data records. The UCD-MPSL database is backed up on a weekly basis.

Original raw data sheets and duplicates are stored in separate locations at MPSL. Excel data files are stored as original and back-up electronic files. All data are compiled, analyzed, and transmitted by Bryn

Phillips (UCD-MPSL), and he is responsible for overall data quality review. Data software is maintained by the SWAMP Data Management Team (DMT) as described in Section B10 of the SWAMP QAPrP.

GROUP C: ASSESSMENT AND OVERSIGHT

20. ASSESSMENTS & RESPONSE ACTIONS

All raw and statistical analysis data are subject to a 100% check for accuracy by the UCD PM and Laboratory QA Officers, who in turn have the authority to issue stop work orders if needed. Data are analyzed and proofread for accuracy, and then QA checked against the QAPP and SWAMP criteria before being entered into the SWAMP database. Original hard copies of the data are filed in a secure cabinet until requested by the PM and/or inclusion into the Final Report. Electronic copies are stored and backed up by each analyst and respective laboratory internal PM.

If corrective action is warranted after UCD-MPSL has performed QA/QC review of the monitoring data, a subcontracting analytical laboratory may be asked to re-analyze samples that did not meet expected project MQOs. Archived samples, maintained by MPSL, may be used to provide additional sample for reanalysis. Corrective actions that result from a project assessment will be documented in the reports.

Assessment of routine laboratory quality control is made on a daily basis, with immediate resolution and corrective action for any discrepancies from targets. These routine quality control assessments include checks of refrigerator and constant room temperatures, precision and accuracy of ancillary toxicity testing measurements (e.g., DO, pH), and culture conditions for test organisms. These routine QC assessments and corrections are made by laboratory staff under the supervision of Bryn Phillips.

Assessments of toxicity test acceptability are made by Bryn Phillips on the day that tests are completed. These include assessments of test control performance, variability among replicates, and acceptability of test conditions of temperature and DO. Corrective actions include repetition of toxicity tests having unacceptable control performance and evaluation of test condition variation relative to test performance. For example, small test-wide exceedences of temperature ranges may be flagged, but the toxicity data may still be used for the project if control response is acceptable; as opposed to using minor fluctuations in test condition as cause to repeat the test. All such decisions will be made in consultation with the PM.

21. REPORTS TO MANAGEMENT

Interpretive Reports will be written and submitted by the UCD PM (John Hunt) to the State Board Contract Manager, Karen Larsen. The Interpretive Report covering data from samples collected during the first field year of the program will be submitted by October 31, 2010. After this initial report, Biannual Interpretive Reports will be due on December 31st of alternating years. Reports will be submitted to the contract manager in electronic format. Sediment chemistry and toxicity data will be submitted to the SWAMP database. The reports will be received by Karen Larsen, who will distribute them to others in the State Water Resources Control Board.

GROUP D: DATA VALIDATION AND USABILITY

22. DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

Data generated for the field monitoring component of this project will be reviewed by the UCD-MPSL PM and QA Officer, and compared against the MQOs and the QA/QC practices cited in the SWAMP QAPrP. When warranted, reanalysis of sample material may be requested of the labs or data will be qualified appropriately.

23. VERIFICATION AND VALIDATION METHODS

SWAMP SOPs *Field Data Verification of the Surface Water Ambient Monitoring Program Database*, *Data Loading and Verification of the Surface Water Ambient Monitoring Program Database*, and *Toxicity Data Verification of the Surface Water Ambient Monitoring Program Database* will be followed. Field monitoring data received at UCD-MPSL will be processed by Bryn Phillips at UCD-MPSL. Any issues discovered during the verification and validation of the data that cannot be resolved will be documented via flags in the SWAMP database and discussed in the bi-annual interpretive reports and fact sheets. Data reporting formats and expectations are written into all sub-contracts. Cover letters and data reports must accompany each data submission, which is verified and validated visually against the original contractual agreement (e.g. total number of samples and parameters to be measured, compliance with data quality indicators, and project objectives). Bryn Phillips of UCD-MPSL will receive and review data from UCD-MPSL and MLML-MPSL, and identify any data quality issues

If issues are identified, they will be resolved through discussions among the principles identified in Table 1. Resolution will include re-sampling or re-analysis of samples if data quality issues cannot be resolved at the data transfer or data base level.

24. RECONCILIATION WITH USER REQUIREMENTS

The first null hypothesis to be tested is that there will be no change over time in either the concentrations of contaminants or the occurrence of toxicity in downstream reaches of streams that receive waters from large watersheds. The first hypothesis will be tested by examining graphical presentations of the changes over time in toxicity and chemistry data from each site and from the overall population of sites, and by conducting statistical tests that quantify the significance of observed changes over time. Long-term trend analyses will be conducted to detect the direction, magnitude, and significance of change over time.

The second null hypothesis to be tested is that there will be no correlation between the concentration of contaminants or occurrence of toxicity on the one hand, and patterns of land use or management activity on the other hand. This hypothesis will be tested by using geographical information system tools to extract land cover data for project watersheds from existing data sets (such as the National Land Cover Dataset [NLCD]). Relationships between land use and stream contamination and toxicity will be evaluated using step-wise multiple regression and other appropriate techniques.

Uncertainty in project findings will be evaluated by using statistical tests to determine the probability that the null hypotheses are falsified. Limitations related to data availability and capture time (as with the NLCD), the ability to quantify levels of management activity in target watersheds, and the size of the project data set will be highlighted in the report as recommendations for future work by this project and others.

Data will be reported in the SWAMP Sediment Database 2.5. Data that do not meet the MQOs in the SWAMP QAPrP will be flagged accordingly. Rejected data will not be included in data analyses while data flagged as estimated will be evaluated for inclusion on a case-by-case basis in conjunction with the associated QA data and program objectives.

APPENDIX A

Marine Pollution Studies Laboratory (MPSL) – Granite Canyon

**Standard Operating Procedures (SOPs) for
Conducting Field Collections of Bed Sediment Samples
at Watershed Integrator Sites
in the Surface Water Ambient Monitoring Program (SWAMP)
Stream Pollution Trend (SPoT) Program**

The SOPs below are for reference and information purposes only, the documents are not required by the Surface Water Ambient Monitoring Program (SWAMP). Please see the SWAMP Quality Assurance Management Plan (<http://www.swrcb.ca.gov/swamp/qamp.html>) for more information regarding SWAMP QA/QC requirements.

Table of Contents

Fundamental Considerations	26
Field Data Sheets	26
Notes To Standardize Swamp Field Data Sheets	27
Site Summaries	28
Bed Sediment Sample Collection	28
General Procedure For Collection Of Bed Sediment	29
A. Hand Core Method – Primary Method For Shallow Streams	30
B. Sediment Scoop Method – Alternate Method For Shallow Streams With Debris	30
C. Sediment Grab Method — Alternate Method For Deeper Waters	31
General Procedure For Processing Of Bed Sediment Samples, Once They Are Collected	32
Transport Of Sample Jars	32
Sediment Homogenization, Aliquoting And Transport	32

Field Collection Procedures for Bed Sediment Samples in the SWAMP Stream Pollution Trends (SPoT) Program

Fundamental Considerations

1. The SWAMP program for Stream Pollution Trend (SPoT) Monitoring at Watershed Integrator Sites is based on the concept that sediment collected from stream depositional areas serves as an indicator of recent pollutant mobilization throughout the upstream watershed. It is therefore critical that sediments are collected from multiple streambed areas where active deposition occurs. Field crews must be well acquainted with stream geomorphology to distinguish between areas of recent deposition (within the past year), and areas where benches, failed banks, or other features indicate older deposits.

2. Contaminants washed from watershed surfaces predominantly adsorb to and are transported with fine particulate matter. Thus it is also critical, for contaminant detection and method standardization over time, that only fine grained sediments are sampled. Ideally, only fine sediments (less than 64 μm in diameter) would be collected. In practice, the target is for fine-grained sediments to make up more than 50% of the sample ($> 50\%$ fines). Before collection, sediment grain size should be checked in the field. Sediment that feels smooth when rubbed between gloved fingers is preferred, and sediment that feels gritty should be rejected unless finer sediment is unavailable in depositional areas at suitable integrator sites.

If suitable depositional areas for collecting sediments cannot be found at a target site, the project scientist (John Hunt or designee) may decide to search the general area for an alternate integrator site where fine sediment is deposited. If an alternate location is sampled, the project scientist will notify collaborating institutions (Regional Monitoring Coordinators, stormwater agencies, etc.) of the change in location. This may result in renaming of the site, and may affect trends analyses. If no suitable depositional areas can be found, sampling personnel should not collect the sediment sample, and should discuss alternatives with the project scientist and collaborators. In this case, a note is added to the cruise report so that the missing sample is accounted for in the reconciliation of monitoring events. Sites that are routinely difficult to collect should be considered for elimination or relocation from the sample schedule, if appropriate.

Field Data Sheets

Field data sheets are used to record specific information about site location, number of depositional areas sampled, types of analyses to be conducted, collection method, photograph identification, and other information. Field data sheets are provided through the Marine Pollution Studies Laboratory website at: <http://mpsl.mlml.calstate.edu/swdwnlds.htm>. Click on the *Field Data Sheets* for the most recent versions. There are guidelines provided below to standardize what is recorded on all data sheets and that should be helpful in completing each form. The entries discussed below and on the field data sheets are recorded at each sampling site.

Notes to Standardize SWAMP Field Data Sheets

(For in the field use)

Key Reminders to identify samples:

1. **Sample Time** is the SAME for all samples (Water, Sediment, & Probe) taken at the sampling event. Use time of FIRST sample as it is important for the chain of custody (COC).
2. **Left Bank/Right Bank**
Left bank is defined as the bank to the left of the observer when facing downstream, and the *right bank* is to the right of the observer when facing downstream

FIELD OBSERVATIONS: (each one of these observations has a *Comment* field in the database so use comment space on data sheet to add information about an observation if necessary)

1. **DOMINANT SUBSTRATE:** if possible; describe DOMINANT substrate type; use UNK if you cannot see the dominant substrate type
2. **WADEABILITY:** in general, is the water body being sampled wadeable to the average person AT the POINT of SAMPLE
3. **PHOTOS:** Digital photos are taken to help document the actual sampling site. The convention is to take photos facing DOWNSTREAM, overlooking the site. Right bank and left bank are thus defined in this downstream-facing direction. Document any discrepancies from this convention. Only one photo is necessary if both left and right banks fit into one frame. Record all photos in the field data sheet space to record picture numbers given by camera; be sure to rename accordingly back in the office. All photos should be renamed and saved with the StationCode_yyyy_mm_dd_uniquecode (e.g. 123ABC123_2007_07_01_BBDS).

SAMPLE DETAILS:

1. **EVENT TYPE:** Note the event type based on which type of media is being collected. For integrator sites, this will always be “WQ.”
2. **PERSONNEL:** First initial and last name (J. Smith, S. Ride). The first person listed is crew leader.
3. **TARGET LAT/LONG:** Refers to the existing station location that the sampling crew is trying to achieve; can be filled out prior to sampling
4. **ACTUAL LAT/ LONG:** is the location of the current sample event. Record coordinates for both upstream extent of sampled reach [Pt1 (U/S)] and downstream extent of sampled reach [Pt2 (D/S)]
5. **OCCUPATION METHOD:** Circle descriptor of how the site is accessed.
6. **SAMPLE TYPE:** For integrator sites, this will always be “Integrated.”
7. **NUMBER OF CONTAINERS FILLED:** Record the number of containers filled for each analysis type.
8. **DEPOSITIONAL AREA SAMPLE INFORMATION:** For each depositional area sampled, circle the appropriate notations in each column. “Under” indicates sediment was submerged; “P” = present; “A” = absent; the “DepthCollec” is the thickness of the sediment layer removed; “SS” = stainless steel; “PC” = polycarbonate; “PE” = polyethylene.

9. **COMMENTS:** In the comments box, draw a rectangle to indicate the shape of the reach sampled, and mark an “x” within it to show the approximate distribution of depositional areas sampled. Record the approximate average water depth, and add any comments about observed inputs or conditions that might affect sediment quality.

Site Summaries

After each field survey, text describing the following characteristics of the site and collection process should be recorded for the cruise report:

1. **Site location:** Provide details (beyond lat longs and other information on the field data sheet) that would allow future field crews or analysts to understand the nature of the sediment sampled, such as water depth, flow, and whether sediment was collected under a bridge, behind an obstruction, within vegetation patches, inside bends, etc.
2. **Access:** Provide information to help with future access, such as contact information for permissions, information about gates and locks, specific location of access paths, etc.
3. **Representativeness of depositional areas:** Since sediment deposition depends on stream morphology, not all streams will allow collection of sediment from multiple areas along a 100 meter reach. If sediment is collected from other types of depositional areas, the configuration of the depositional area(s) sampled should be described, and a justification should be given as to how the sampled area is expected to contain the range of fine material representative of that generally transported by the stream over the target time period.

Bed Sediment Sample Collection

If samples of water and bed sediment (hereafter termed "sediment") are taken in the same reach, water samples are collected first. Care must be taken not to sample sediments that have been walked on or disturbed in any manner by field personnel. Sediment samples from all depositional areas within a site are placed into the same 4-liter composite jar, which is filled at least three quarters full. Once all depositional areas at a site have been sampled, the jar is sealed and placed on ice in a cooler. Once sample jars arrive at MPSL, they are thoroughly homogenized, and then aliquoted into separate jars for chemical or toxicological analysis. Sediment samples for metals and organics are submitted to the respective analytical laboratories in separate glass jars, which have been pre-cleaned according to laboratory protocol.

Labeling

Label the jars with the station ID, sample code, matrix type, project ID, time, and date of collection, as well as the type of analysis requested (e.g., metals, conventionals, organics, or archives).

Characteristics of Ideal Sediment Material to be Collected

Many of the chemical constituents of concern are adsorbed onto fine particles. One of the major objectives in selecting a sample site, and in actually collecting the sample while on site, is to obtain recently deposited fine sediment, to the extent possible. Avoid hard clay, bank deposits, gravel, disturbed and/or filled areas. In following this guidance, the collection of sediment is purposefully being biased for fine materials, which must be discussed thoroughly in any subsequent interpretive reporting of the data, in regards to representation of the collected sample to the environment from which it was collected.

Characteristics of an Ideal Site

Quiescent areas are conducive to the settling of finer materials (EPA/USACOE, 1981). Within the 100-meter reach of the site, choose depositional areas with lower hydrologic energy, such as the inner (depositional) side of bends or eddies where the water movement may be slower. Impoundments, reservoirs and estuaries are also generally depositional environments.

Selecting the Appropriate Sediment Type for Analysis Sediment will vary from site to site and can vary between sample events at a particular site.

Streams and Rivers: Sediment collection in flowing streams is often a challenge. In areas of frequent scouring there may not be sufficient sediment for collection during or following periods of high flow. Sediment collection during these times may prove unsuccessful and may have to be rescheduled or cancelled.

More often than not, a dredge or mechanical grab device does not function well for collection of sediment in smaller streams. In many cases, sediment will have to be collected using a pre-cleaned polyethylene scoop or polycarbonate core tube. Collect the top 1 to 5 cm for analysis, depending on the homogeneity of the sediment. If the sediment exhibits clear layering, collect only the upper-most layer. If the sediment appears vertically homogeneous, the entire top 5 cm may be collected. Sediment is collected from 5 to 10 depositional areas within a 100-m reach and these are composited within the sample jar.

Reservoirs, ponds, and other impoundments: Collect the top 1 to 5 cm for analysis, as above. Five to 10 grabs are composited for the sediment sample, with grabs spaced within an area comparable to a 100 meter reach that would be expected to yield fine sediment representative of that transported by the stream.

General Procedure for Collection of Bed Sediment

After choosing appropriate depositional areas within the site reach, collect the sample using one or more of the following procedures, depending on the setting. Access to the sediment often depends on the type of protective clothing worn by field crews. Field crews generally wear chest waders. Wet suits and other diving gear are generally avoided due to hygiene considerations in contaminated streams. When crews can reach the stream bottom with their hands (without diving), short core tubes are preferred. When water is more than about half a meter deep, longer cores tubes are preferred. Core tubes are preferred over scoops because tubes minimize the loss of fine material from the sediment surface. Scoops may be used when debris makes cores ineffective, or when sampling dry or damp sediment that is no longer submerged. Grabs are used when water is too deep to wade, or when long cores are ineffective.

The goal is to collect the top 1 to 5 cm of recently-deposited fine sediment only. Survey the sampling area for appropriate fine-sediment depositional areas before stepping into the stream, to avoid disturbing possible sediment collection sub-sites. Carefully enter the stream and start sampling at the closest appropriate reach, then continue sampling UPSTREAM. Advancing downstream may in some cases lead to sampling disturbed sediment.

A. Hand Core Method – primary method for shallow streams

1. Short cores

- The short hand core sampler consists of a 10-cm-diameter polycarbonate core approximately 50 cm long.
- One method of using short core tubes is to:
 - a. push the tube vertically into the sediment to beyond the desired sample depth,
 - b. cap the bottom with a polyethylene core cap or by placing their gloved hand underneath the tube to hold the sediment in place,
 - c. pull the core out of the sediment,
 - d. slowly decant off overlying water,
 - e. push the sediment out of the tube, discarding all but the top 5 cm (or less), and
 - f. place the remaining surficial sediment in the collection jar.
- A second method for using short core tubes is to slide the tube horizontally along the sediment, with the bottom edge 5 cm or less below the sediment surface. The core is thus used as a scoop, but has better control and retention of fine surficial material. Both ends of the core are then covered with gloved hands, the core is raised out of the water, overlying water is slowly decanted off, and the sediment sample is placed in the jar.

2. Long cores

- The long hand core sampler consists of a 5-cm-diameter polycarbonate core approximately 1.5 meters long.
- To collect samples with a long core:
 - a. push the tube vertically into the sediment to beyond the desired sample depth,
 - b. cap the top of the core with a gloved hand to create suction,
 - c. pull the core out of the sediment,
 - d. slowly decant off overlying water,
 - e. push the sediment out of the tube, discarding all but the top 5 cm (or less), and
 - f. place the remaining surficial sediment in the collection jar.

B. Sediment Scoop Method – Alternate Method for Shallow Streams with Debris

In situations where the target fine sediment is found among plants, rocks, sand, shells, or other debris, a scoop may be the best way to collect. Use a separate pre-cleaned polyethylene scoop for each site. The same scoop may be used for multiple depositional areas within a site. Push the scoop up to 5 cm below the sediment surface, and gently slide it along until it is just full of sediment. Place a gloved hand over the sediment as the scoop is brought to the water surface to minimize loss of fine material. Place the sediment into the collection jar.

In situations where adequate depth and quantities of homogeneous fine sediment is found beneath mats of vegetation, the sediment may be scooped with a gloved hand, brought to the surface, and placed in the jar. If necessary, vegetation and other debris may be removed with a gloved hand.

C. Sediment Grab Method — Alternate method for deeper waters.

Description of sediment grab equipment:

- A mechanical sediment grab such as a stainless steel “Young-modified Van Veen” or “Petite Ponar” is suitable.
- The mechanical grab is deployed primarily from a boat, and is used in deeper, non-wadeable waters.
- It is also deployed by field personnel from land in settings which allow its use: primarily from bridges; from smaller vessels in deep streams or drainage channels.
- Smaller grabs (e.g. Petite Ponar) may be deployed while wading in channels if necessary.

Deploying and retrieving the grab:

- Slowly lower the grab to the bottom with a minimum of substrate disturbance.
- Retrieve the closed dredge at a moderate speed (e.g., less than two feet per second).
- Upon retrieval, open the lids of the sediment grab, examine the sample to ensure that the sediment surface is undisturbed, that fine-grained material has been collected, and that the sample should not be rejected.

Rejection Criteria—reject the sample if the following are not met:

- Mud surface must not be pressing out of the top of the sampler. If it is, lower the grab more slowly.
- Overlying water must not be leaking out along the sides of the sediment in the grab. This ensures the surficial sediment is not washed out.
- Sediment surface is flat and level in the sampler. If it is not level, the grab has tilted over before closing.

Processing the sediment sample from the grab equipment:

- The water overlying the sediment in the grab is very gently decanted by slightly tipping the grab with the lid closed until the water runs out the top.
- The decanting process should remove all of the overlying water but not remove the surficial sediments. The laboratory reports percent water for the sample, so overlying water is not included in the sample container.
- The sediment is examined for depth of penetration, color and thickness of top aerobic zone, and texture. These observations are recorded in the logbook.
- Use a pre-cleaned polyethylene scoop to collect the top 1 to 5 cm from at least five sub samples, and otherwise, exclude the bottom-most layer.

Cleaning the Grab Equipment and Protection from Potential Contaminating Sources:

- The sediment sampler will be cleaned prior to sampling EACH site by: rinsing all surfaces with ambient water, scrubbing all sediment sample contact surfaces with Micro™ or equivalent detergent, rinsing all surfaces with ambient water, rinsing sediment sample contact surfaces with 5% HCl, and rinsing all sediment sample contact surfaces with methanol.
- The sediment grab will be scrubbed with ambient water between successive deployments at ONE site, in order to remove adhering sediments from contact surfaces possibly originating below the sampled layer, thus preventing contamination from areas beyond target sampling area.

- Sampling procedures will attempt to avoid exhaust from any engine aboard any vessel involved in sample collection. An engine will be turned off when possible during portions of the sampling process where contamination from engine exhaust may occur. It is critical that sample contamination be avoided during sample collection. All sampling equipment (e.g., siphon hoses, scoops, containers) will be made of non-contaminating material and will be appropriately cleaned before use. Samples will not be touched with un-gloved fingers. In addition, potential airborne contamination (e.g., from engine exhaust, cigarette smoke) will be avoided.

General Procedure for Processing of Bed Sediment Samples, Once They Are Collected

Transport of Sample Jars

- Single bag all sediment containers to prevent cross contamination.
- Make sure all containers are capped tightly and stored in a cooler on cube ice at 4 °C.
- Check cooler temperature and record in log book every 8-12 h or whenever sampler suspects that the temperature has not been maintained at 4 °C.

Sediment Homogenization, Aliquoting and Transport

Sediment samples from the multiple depositional areas within a reach may be put in the collection jar, sealed, and placed in coolers for transport without field homogenization. Immediately place the labeled jar on ice, cool to 4 °C, and keep in the dark at 4 °C until delivery to the laboratory. Once samples arrive at the laboratory, the sediment in the container is homogenized and aliquoted. All sample identification information (station numbers, etc.) will be recorded prior to homogenizing and aliquoting. The sample is stirred with a polyethylene scoop or spoon for at least 2 min, but longer if necessary, until sediment/mud appears homogeneous. The sediment sample is then aliquoted, using a clean plastic scoop, into appropriate containers for trace metal chemistry, organic chemistry, and toxicity testing, as described in the table below.

Summary of Sample Container, Volume, Preservation, and Storage Requirements for Bed Sediment Samples (for contaminant analysis)

Parameters for Analysis	Recommended Containers	Typical Sample Volume (mL)	Initial Field Preservation	Maximum Holding Time
Bed Sediment Samples				
Trace Metals, including Hg and As (except for Se--see below)	60-mL I-Chem 300- series clear glass jar with Teflon lid-liner; Pre-cleaned	60 mL (one jar)	Cool to 4 °C, dark, up to 14 days	12 months ⁽¹⁾ (-20 °C)
Selenium (separate container required)	60-mL I-Chem 300- series clear glass jar with Teflon lid-liner; Pre-cleaned	60 mL (one jar)	Cool to 4 °C, dark, up to 14 days	12 months ⁽¹⁾ (-20 °C)
Synthetic Organic Compounds	250-mL I-Chem 300-series amber glass jar with Teflon lid-liner; Pre-cleaned	500 mL (two jars)	Cool to 4 °C, dark, up to 14 days	12 months ⁽¹⁾ (-20 °C)
Sediment TOC	250-mL ⁽³⁾ clear glass jar; Pre-cleaned	125 mL (one jar)	Cool to 4 °C, dark, up to 28 days	12 months ⁽²⁾ (-20 °C)
Sediment Grain Size	250-mL ⁽³⁾ clear glass jar; Pre-cleaned	125 mL (one jar)	Cool to 4 °C, dark, up to 28 days	28 days (4 °C) <i>Do not freeze</i>
Sediment Toxicity Testing	1-L I-Chem wide-mouth polyethylene jar with Teflon lid-liner; Pre-cleaned	2 (two jars filled completely)	Cool to 4 °C, dark, up to 14 days	14 days (4 °C) <i>Do not freeze</i>
<p>(1) Sediment samples for parameters noted with one asterisk (*) may be refrigerated at 4 °C for up to 14 days maximum, but analysis <u>must</u> start within the 14-day period, or the sediment sample <u>must</u> be stored frozen at minus (-) 20 °C for up to 12 months.</p> <p>(2) Sediment samples for sediment TOC analysis can be held at 4°C for up to 28 days, and <u>should</u> be analyzed within this 28-day period, but can be frozen at any time during the initial 28 days, for up to 12 months at minus (-) 20 °C.</p> <p>(3) Sediment samples for TOC AND grain size analysis can be combined in one 250 mL clear glass jar, and sub-sampled at the laboratory in order to utilize holding time differences for the two analyses. If this is done, the 250 mL combined sediment sample must be refrigerated only (<u>not frozen</u>) at 4 °C for up to 28 days, during which time the sub-samples must be aliquoted in order to comply with separate storage requirements (as shown above).</p>				

APPENDIX B MPSL Chain of Custody Form

University of California, Davis - Marine Pollution Studies Laboratory

Chain of Custody

34500 Coast Route One
Monterey, CA 93940

Contact: Bryn Phillips
Phone: 831-624-0947

Final Destination:

Contact:
Phone:

Sample Name	Sample ID Number	Date Sampled	Analysis	Quantity			

	Date	Signature	Time	Location
Relinquished by:				
Received by:				
Relinquished by:				
Received by:				
Relinquished by:				
Received by:				

APPENDIX C MPSL Sampling Equipment Cleaning SOP

SAFETY STANDARDS AND PROTOCOLS

Scrubbing Lab Ware

- Wear Nitrile gloves, lab coat.

Acetone or Hexane Usage

- Wear rubber gloves, blue plastic suit, apron, rubber boots, full-face respirator with organic vapor/particulate cartridges. Turn on fume hood and open window.
- All plastic containers contaminated with sediment or water samples, and lab ware of unknown origin are treated with hexane. All glass containers are treated with acetone.
- Use labeled squirt bottle to apply solvent. Dump used solvent into a collection beaker.
- When beaker is full, dispose of used solvent in transfer bottle. At the end of the session, transfer used solvent to drum.
- DO NOT pour solvent down the sink (small amounts of residual solvent are okay).
- Rinse solvent bottles thoroughly, cross out label, and store for recycling. Discard caps.

Acid Rinsing/Soaking Lab Ware:

- Wear rubber gloves, lab coat, apron, rubber boots, face shield.

Discarding Used Acid

- Wear rubber gloves, lab coat, apron, rubber boots, face shield. Turn on exhaust fan in neutralizing room and open door.
- Before draining acid baths, check “old acid” bottles; at least two should be full. Acid-rinse any acid-only containers. Also confirm that acid neutralization bin is empty, and that there is NaOH in stock.
- Drain acid baths after their third full use (this is considered “old acid”).
- Drain and neutralize one acid bath at a time.
- Neutralize acid with solid NaOH. CAUTION!!! This substance is highly corrosive and will burn skin.
- Add small amounts of NaOH, stirring to prevent caking.
- Adjust acid until pH is between 6 and 9.
- Drain neutralizing tank to treatment system (open drain valve only half-way). Close valve when drained.
- Do not hold un-neutralized acid in bin overnight.

Mixing New Acid

- Wear rubber gloves, lab coat, apron, rubber boots, full-face respirator. Turn on fume hood and open window.
- NEVER ADD WATER TO FULL-STRENGTH ACID!
- Fill emptied acid bath half-full with DI water.
- Carefully add 1.5 bottles of concentrated HCl to bath. Top off with DI water to line marked “1.5”.
- Rinse acid bottles thoroughly, cross out label, and store for recycling. Discard caps.
- Pipette Baths - acid should be replaced in these baths every 200 pipettes. Fill one pipette bath with old acid, the other with 0.5 bottle of concentrated HCl and deionized water.

CLEANING LAB WARE

1) Basic Lab Ware Procedure (all containers contaminated with sediment or water samples, e.g. beakers, jars, flasks, core tubes, orange caps, centrifuge tubes; containers of unknown origin; various lab ware contaminated with chemicals or samples; bottle caps; lid liners).

- Scrub with dilute Micro solution and rinse well with DI water. Remove any taped-on site labels. Make sure that all traces of dirt are removed.
- Rinse with solvent. Use hexane for plastics or acetone for glass. Jars, bottles, flasks, beakers and cylinders only need the inside rinsed. All other lab ware should have all surfaces rinsed.
- Rinse well with DI water.
- Soak 24 hours in acid bath. For plastic items, make sure they sit overnight to vent before they go into acid. Make sure that all surfaces are covered with acid (eliminate air bubbles, if necessary, and don't stack one item in another unless they float). NOTE: metal items only get swirled in acid, then rinsed and placed in DI bath.
- Rinse well with DI water.
- Soak 24 hours in fresh DI bath. Make sure that all surfaces are covered with water (eliminate air bubbles, if necessary, and don't stack one container in another unless they float).
- Rinse with DI water. (NOTE: Amber bottles and 50-ml glass beakers need a final distilled water rinse.)
- Place in drying oven overnight. Put away when dry (numbered containers go in order). Make sure that containers are upside-down, capped, covered, or bagged as appropriate, and that site labels are removed.

2) Plastic Ware Procedure (for plastic and glass containers and pipettes used in metals or ammonia tests only, i.e. ACID ONLY)

- Rinse with DI water.
- Rinse with old acid (dunk in acid bath that needs to be drained, or fill separate container with old acid from a bottle; dump acid in neutralizing bath when done).
- Rinse with DI water.
- Soak 24 hours in acid bath. Make sure that all surfaces are covered with acid (eliminate air bubbles, if necessary, and don't stack one container in another unless they float).
- Rinse well with DI water.
- Soak 24 hours in fresh DI bath. Make sure that all surfaces are covered with water (eliminate air bubbles, if necessary, and don't stack one container in another unless they float).
- Rinse with DI water.
- Place in drying oven overnight. Put away when dry. Make sure that containers are upside-down, capped, covered, or bagged as appropriate, and that site labels are removed.

3) Screen Tubes

- Gently scrub with Micro solution and rinse well with DI water. Dry overnight before hexane.
- Dip entire dry screen tube into beaker of hexane.
- Rinse well and promptly to avoid melting glue.
- Soak in acid bath for 20 minutes. Acid should flow through screen when removed.
- Rinse well with DI water.
- Soak 24 hours in fresh DI bath.
- Soak 48 hours in 1-micron filtered running seawater.
- Rinse well with distilled water.
- Place in drying oven overnight. Make sure that screens are bagged by mesh size, and that site labels are removed.

4) Jar Lids (from I-Chem-type sample jars, typically ≥ 250 ml)

- Remove liners and wash separately as in #1. When rinsing with hexane, stack liners in a beaker, pour hexane over them, and swirl.
- Scrub lids extremely well with a toothbrush and Micro solution. Be sure to clean all mud out of threads and grooves. Rinse well with DI water.
- Place in drying oven.
- When dry, check that lids are clean, remove all site labels, fit with clean liners, and screw onto jars. If jars are still dirty, place lids and liners in separate zip-lock bags.
- Plastic jars are fitted with non-Teflon liners. Glass jars are fitted with Teflon liners.

5) Volumetric Pipettes

- Follow procedure 1 or 2. Pipettes go in bath tips-up.
- Large quantities of pipettes can be washed in the pipette baths.